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EFFECT OF OXYGEN ON THE IGNITION OF LIQUID FUELS

By H. Pahl

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EFFECT OF OXYGEN ON THE IGNITION OF LIQUID FUELS.*

By H. Pahl.

Introduction

The ignition temperature, ignition lag, and ignition strength of simple and homogeneous fuels in combustion air of small oxygen content differ from what they are in air of greater oxygen content. In the case of small oxygen content, these fuels behave as if mixed unevenly. In the case of air with a definite oxygen content, the simple fuels have two ignition points, between which ignition takes place within a certain temperature range. The phenomena are explained by pyrogenous decomposition, comparison of the individual heat quantities, and the effect of the walls.

Apparatus (Figure 1)

The bottle a is filled partly with air and partly with the desired quantity of oxygen. The water, flowing out of the bottle b, forces the mixture of gases through the finely adjustable three-way cock c, into the wash bottle d, or into the absorption vessel e. After being washed, the mixture is

*"Einfluss des Sauerstoffs auf die Zündung flüssiger Brennstoffe" in Zeitschrift des Vereines deutscher Ingenieure," June 16, 1928, pp. 857-860.

dried in the calcium chloride tube f and heated in the copper tube g before it reaches the ignition block k and the combustion chamber v (Fig. 2). The opening in the plug of the ignition block, through which the combustible mixture is introduced, is made as small as possible, so that the mixture of air and oxygen will not be diluted with extraneous air. The fuel falls in small drops from the movable dropping tube h (Fig. 1), into the combustion chamber v (Fig. 2). The ignition block is electrically heated, the temperature in the block and in the combustion chamber being measured with the aid of an iron-constantan thermocouple. The ignition block is similar to the Krupp ignition-point tester.* It is, however, larger than the latter so that a sufficient amount of oxygen is always available even when experimenting with air. The capacity of the combustion chamber is 11 cm³ (0.671 cu.in.) as against 3 cm³ (0.183 cu.in.) in the Krupp ignition tester.

P r o c e d u r e

The experiments were performed in series for a definite oxygen content of the mixture. The barometer stood at about 725 mm Hg. Before and after each series of experiments the oxygen content of the mixture in bottle a was measured by means of

*Otto Alt, "Flussige Brennstoffe und ihre Verbrennung in der Dieselmachine" in V. D. I., July 14, 1923, pp. 686-691. For translation, see N.A.C.A. Technical Memorandum No. 281: "Combustion of Liquid Fuels in Diesel Engine," 1924.

pyrogalllic acid. Both measurements always gave the same result. The mixture was so regulated that about 250 bubbles or 40 cm³ (2.44 cu.in. per minute passed through the washing bottle. The combustion chamber was thoroughly rinsed after each test. In each test it was determined:

1. Whether any ignition at all took place in the combustion chamber at the existing temperature;
2. After how long a time the ignition took place, that is, the ignition lag;
3. The strength or intensity of the ignition.

The series of tests were made with falling temperatures. The heat flow could thus be so regulated that the temperature drop between two consecutive measurements was only a fraction of a degree.

The temperature in the combustion chamber was not measured directly. The temperature difference in the ignition block and in the combustion chamber was measured at the beginning and at the end of each series of tests and also at every 100°C. Only the temperature of the ignition block was read during the delivery of the fuel. The temperature in the combustion chamber was then determined from the above-mentioned temperature differences. The ignition lag was determined by measuring with a stop watch the time elapsed from the instant the drop left the drop-

ping tube to the instant of ignition. This measurement is very inaccurate, although the errors in the great number of tests tend to offset one another.

The strength of the ignition could be determined from the height and color of the ignition flame, although the determination was rendered difficult by personal errors and the shortness of the time available for observation. The height of the flame was reckoned from the bottom of the combustion chamber. The color of the flame was blue for strong ignitions in which violent explosions ensued. As the strength of the ignitions diminished, the violence of the explosions diminished also, and the color changed to white and then to yellow. The height of the flame, calculated on the basis of the blue flame, was therefore chosen as the criterion for the ignition strength, the factor 0.55 being adopted for the white flame and 0.1 for the yellow flame.

In the preliminary tests it was found that the ignition temperature varied several degrees when the velocity of the mixture in the combustion chamber varied. In the main tests, therefore, the mixture was shut off by compressing the tube 1 with the hand during the admission of the fuel from the dropping tube. Furthermore, the quantity of fuel used for each test always had to be the same. The dropper was therefore a finely drawn glass tube furnishing very small drops of about 3 mg (0.000106 oz.) weight.

The investigation covered chemically pure benzene (C_6H_6),

chemically pure allyl alcohol (C_3H_5OH), commercial benzine (Sp. Gr. 0.725 at $15^{\circ}C$) and an American gas oil (Sp. Gr. 0.859 at $15^{\circ}C$). Benzene and allyl alcohol were chosen because they are simple and homogeneous compounds. Benzine and gas oil, on the contrary, are not homogeneous, but are mixtures of several hydrocarbons of high molecular weight.

Experimental Results

In the tests with allyl alcohol, benzine and gas oil, the effect of oxygen on the ignition point, ignition lag and ignition strength was determined. In the case of benzene, due to the high temperatures required, only the effect of the oxygen on the ignition point was investigated. In Figures 3 to 6 each series of experiments with a given oxygen content appears as a vertical line. In the gas-oil tests a indicates partial failure to ignite in these regions. The lower ends of the vertical lines represent the ignition points. Their union forms the ignition curve, which bounds the field of ignition.

In the case of allyl alcohol and benzene the ignition curves are irregular, i.e., the ignition points vary for slight changes in the test conditions. The same is true of benzine and gas oil for a low oxygen content of the mixture. The ignition points of benzine and gas oil, on the other hand, are very stable for a high oxygen content and therefore scarcely affected by changes in the test conditions.

For allyl alcohol and benzene the ignition temperatures rise with decreasing oxygen content, the ignition curves asymptotically approaching the ordinate of zero oxygen content. Benzine (Fig. 5) and gas oil (Fig. 6), behave quite differently. The ignition point of benzine is constant for an oxygen content of 35 to 100%, and of gas oil for an oxygen content of 22 to 100%. The ignition temperature rises with decreasing oxygen content, as in the cases of allyl alcohol and benzene, only for a small oxygen content (21 to 33% for benzine and 21 to 26% for gas oil). This portion of the ignition curve also asymptotically approaches the ordinate of zero oxygen content.

Particularly striking, however, is the behavior of benzine for an oxygen content of 26 to 34% and of gas oil for an oxygen content of 22 to 26%. In these regions ignition takes place regularly down to a certain temperature, below which it is then entirely interrupted for a certain temperature range. Below this range the mixture again ignites regularly, down to a certain temperature, below which no further ignition takes place. The temperature ranges within which the ignition is interrupted become smaller with increasing oxygen content (Figs. 5 and 6).

Figures 7 to 9 represent the ignition lag plotted against the temperature in the combustion chamber for different percentages of oxygen with allyl alcohol, benzine and gas oil. The actual values of the ignition lag are smaller than those entered in the diagram, by the time occupied by the fall of the drops,

which is 0.3 second. During the combustion in the engine the ignition lags are much smaller, due to the very much smaller size of the drops.

According to these results the ignition lag increases for all three fuels with decreasing oxygen content, as well as with decreasing temperature. In the cases of benzine and gas oil, however, the curves are not continuous. With a low oxygen content and high temperatures these fuels behave very differently than with a high oxygen content and low temperatures. In the first case they are like allyl alcohol. The curves spread out like a fan and, at most, reach values of only 2 to 3 seconds. The curves for a high oxygen content and low temperatures, on the contrary, tend toward the ignition axis, thus acquiring a steep slope. The ignition lag is therefore greatly increased in comparison with the ignition temperature, sometimes reaching 15 and even 23 seconds.

In Figures 10 to 12 the flame heights, reckoned on the basis of the blue ignition flame as the measure of the ignition strength for allyl alcohol, benzine and gas oil, are plotted against the temperatures in the combustion chamber. According to these curves the ignition strength decreases in general with the oxygen content, which fact agrees with the increase in the ignition lag. In the cases of benzine and gas oil, however, the curves are bent strongly downward with their lowest values at certain temperatures. For benzine this temperature is about

385°C; for gas oil, about 420°C. With insufficient oxygen the ignition strength becomes negative, that is, the ignition ceases.

The increasing of the ignition strength in the neighborhood of the ignition point for high oxygen content is worthy of note. The ignitions, for benzine and gas oil, in particular, reach their greatest intensity shortly above the ignition temperature. Despite the steep drop of many curves, the transition from the ignition region to the region of no ignition is always gradual. To be sure, the region in which the ignition strength decreases, as, for example, in benzine, often embraces only 1 to 2 degrees. This region becomes greater with the lowering of the oxygen content. In the case of gas oil (Fig. 12) the ignition strength drops so low that with medium oxygen content and up to 2° above the ignition point the flame fails to emerge from the combustion chamber. With a small oxygen content no flame appears below 4° above the ignition temperature, but smoke is ejected from the combustion chamber after a certain interval of time.

With hydrocarbons of high molecular weight, the experiments show that the ignition points and ignition lags behave quite differently for mixtures of low oxygen content than for those of high oxygen content. In mixtures of low oxygen content they behave the same as for the simple compounds, allyl alcohol and benzene. This leads to the inference that hydrocarbons of high molecular weight form hydrocarbons of lower molecular weight by pyrogenous decomposition. Moreover, the ignition-strength

curves indicate a particularly lively decomposition of hydrocarbons of high molecular weight within a certain temperature range.

This decomposition is an endothermic process and therefore requires heat. On the other hand, heat is freed by a flameless oxidation preceding the ignition. That such oxidation takes place is shown by the following consideration. We speak of combustion only when a flame is produced, therefore when a temperature of at least 800°C is reached. The heat for this rise in the temperature of the gases can be produced only by the reaction of carbon and hydrogen with oxygen. If ignition is to take place, the heat liberated by the flameless oxidation must always be greater than the heat necessary for the decomposition of the hydrocarbons.

The more the heat of combustion exceeds the heat required for the decomposition, the stronger the combustion becomes. The smallest values of the ignition strength, as illustrated by the height of the flame in Figures 11 and 12, are therefore explained by the fact that, at these temperatures, very vigorous decompositions occur so that ^{much} heat is absorbed. This fact is corroborated by the results of Rieppel's experiments ("Mitt. über Forschungsarbeiten," published by V. D. I. (Zeitschrift des Vereines deutscher Ingenieure) No. 55, 1908). His steam-pressure lines become vertical in the same temperature region, thus indicating decomposition. If the ignition strength decreases with decreasing oxygen content, then, according to the above hypothe-

sis, the surplus combustion heat must also decrease. This can be explained by the behavior of the combustion air and fuel vapors in the combustion chamber. The greater the oxygen content is, the more vigorously it penetrates the fuel vapors. In the decomposition of compounds of high molecular weight the fuel vapors burn as long as there is any oxygen. The rest then breaks up, into simpler hydrocarbons.

The more oxygen there is present, the greater is the portion of the fuel vapors burned in comparison with the portion which is simply dissociated. At the temperature at which the dissociation is the strongest when the oxygen content is small, the liberated combustion heat no longer suffices to raise the temperature to the combustion point. The smaller the oxygen content is, the greater the temperature range over which the ignition fails.

At high temperatures of the combustion chamber, a portion of the heat of dissociation is furnished by the combustion air or by the surrounding walls. Consequently, a greater portion of the combustion heat is available for heating the gases, and the ignition becomes stronger. At low temperatures, on the other hand, the tendency of the fuel vapors of high molecular weight to dissociate is smaller, and less heat is therefore required for the dissociation, so that the combustion heat is again in excess, and the ignition becomes stronger.

A certain interval of time elapses before the combustion

temperature is reached. The more heat imparted to the surrounding walls, i.e., the colder the combustion chamber, the greater this interval of time becomes. This explains the increase in the ignition lag with falling temperature. The steep slope of the ignition lag shortly above the ignition point is due to the fact that, within this temperature range and up to the ignition point, the portion of the heat used to vaporize the fuel is greater than at high temperatures. In the latter case, dissociation takes place in the vapor hulls first formed around the fuel drops, so that ignition occurs before the fuel is fully vaporized. For this reason, two or more ignitions are obtained in succession at high temperatures, if the oxygen supply is not interrupted. Below the temperature at which the decomposition is the strongest, the latter, and consequently the combustion, proceeds very slowly. Hence there is sufficient time for extensive vaporization. If ignition then takes place, the combustion chamber contains such a large quantity of fuel vapors that the ignition is very violent.

The constancy of the ignition temperature for mixtures of high oxygen content is explained by the fact that below the ignition point the decomposition of fuel vapors of high molecular weight practically ceases. Variations in the experimental conditions can therefore have only a very slight effect on the ignition temperature. This slight effect is due to the fact that the fuel is a mixture of several hydrocarbons.

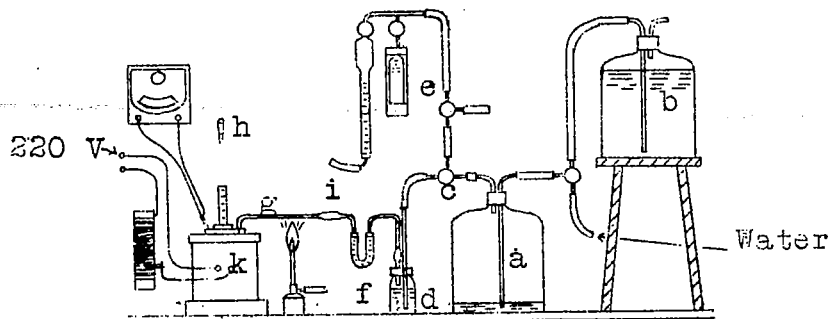
In simple hydrocarbons, decomposition and flameless oxidation occur, to be sure, even below the ignition temperature. This oxidation proceeds very slowly, but is accelerated by raising the temperature of the combustion chamber. Since simple hydrocarbons, especially the saturated ones and those of the benzene series, require more heat for their decomposition than those of high molecular weight and the unsaturated ones, the simple hydrocarbons require a higher ignition temperature, as already verified by Holm (*Zeitschrift für angewandte Chemie* Vol. 26 (1913), p. 273, and by Wollers and Ehmcke (*Kruppsche Monatshefte*, Vol. II (1921))).

The surroundings also greatly affect the ignition process. This explains the vacillating behavior of the ignition temperatures of simple hydrocarbons. Slight variations in the supply of the hot mixture of air and oxygen, or of the fuel or in the size or shape of the combustion chamber, affect the ratio of the heat quantities to one another and consequently the ignition temperature.

With different apparatus quite different ignition temperatures are therefore obtained in the combustion of hydrocarbons of high molecular weight in air, or of simple hydrocarbons in air and oxygen. Comparative tests with a Krupp ignition-point tester have verified this fact. The ignition temperatures thus found differ greatly from the ones given here. On the contrary,

benzine and gas oil in oxygen had almost the same ignition temperatures as those obtained in the present investigation.

Translation by
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Apparatus

- | | |
|-----------------------|---------------------------|
| a, Gas bottle. | f, Calcium-chloride tube. |
| b, Water bottle. | g, Copper tube. |
| c, 3-way cock. | h, Dropper. |
| d, Wash bottle. | i, Rubber tube. |
| e, Absorption vessel. | k, Ignition block. |

Fig. 1

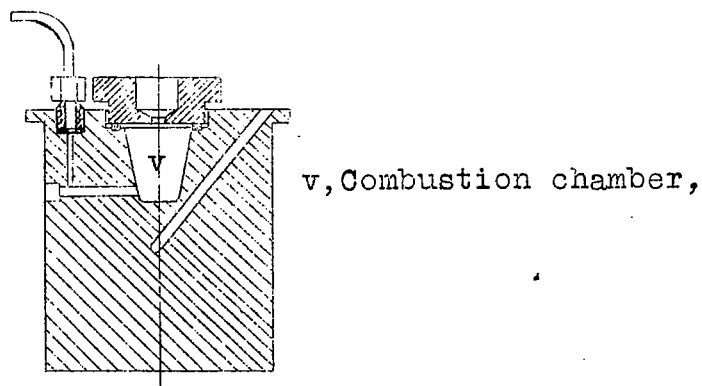


Fig. 2 Ignition block.

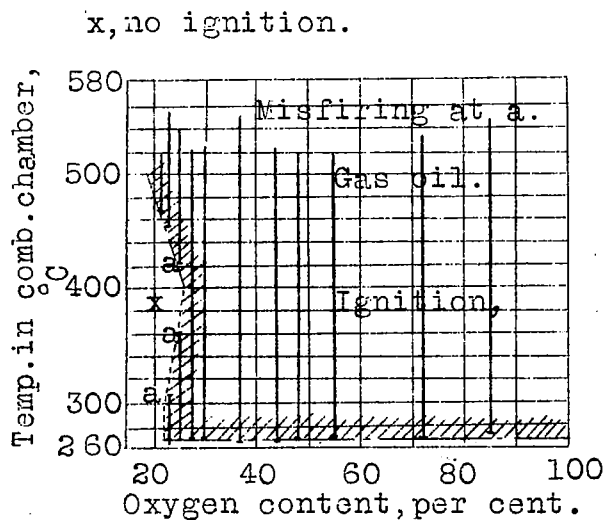
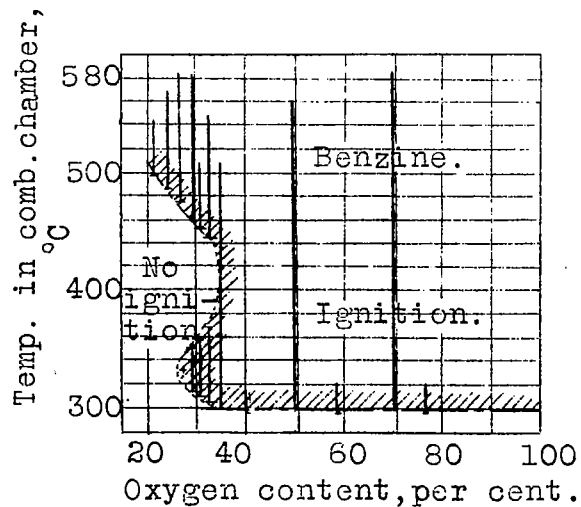
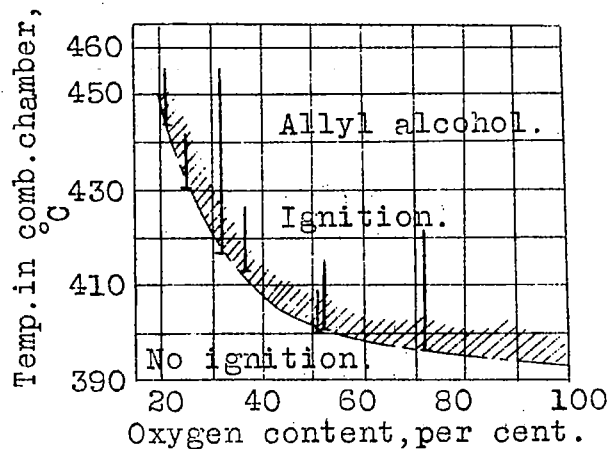
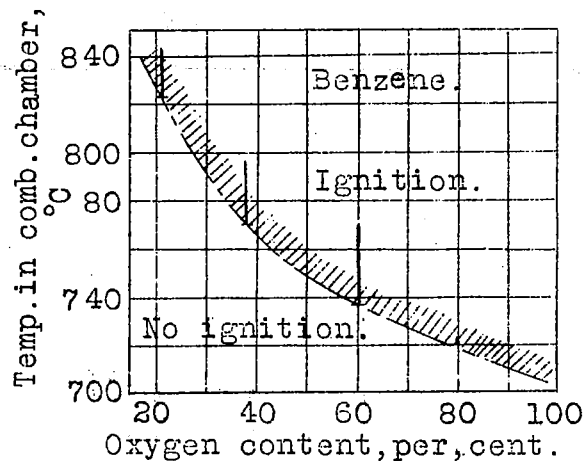
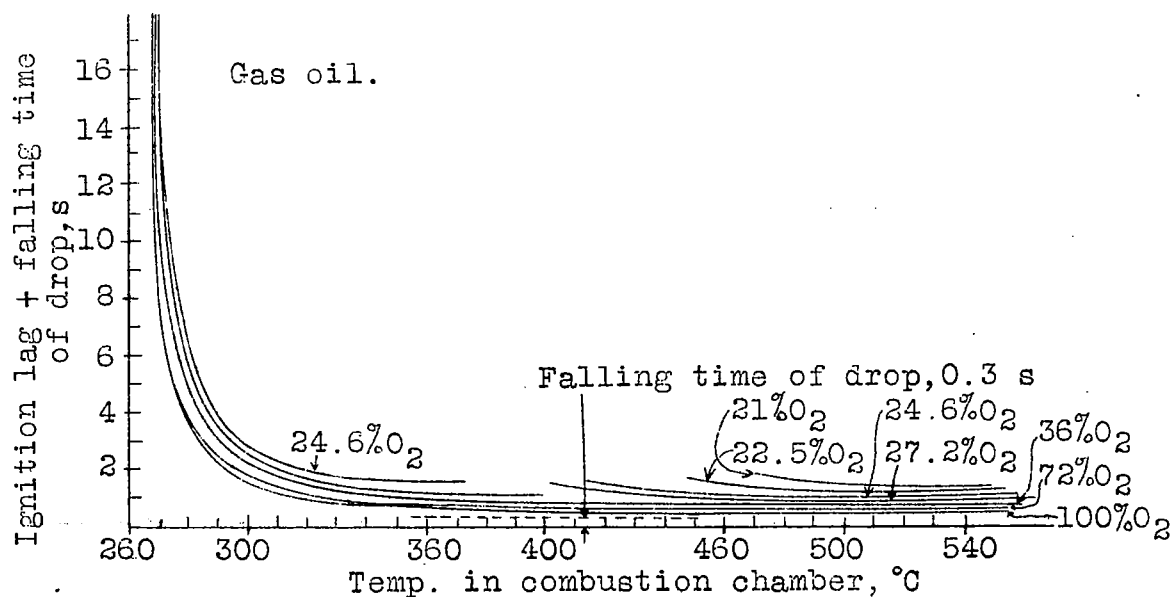
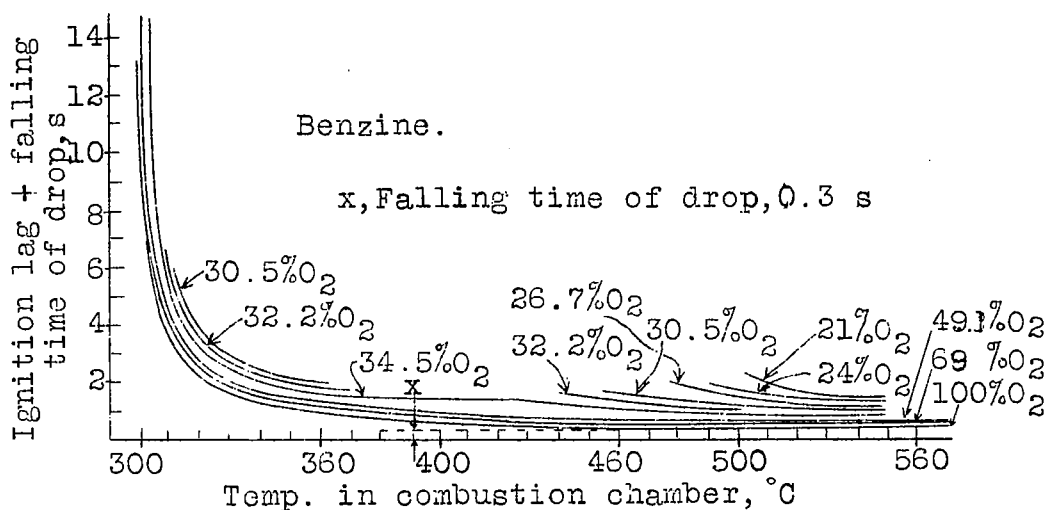
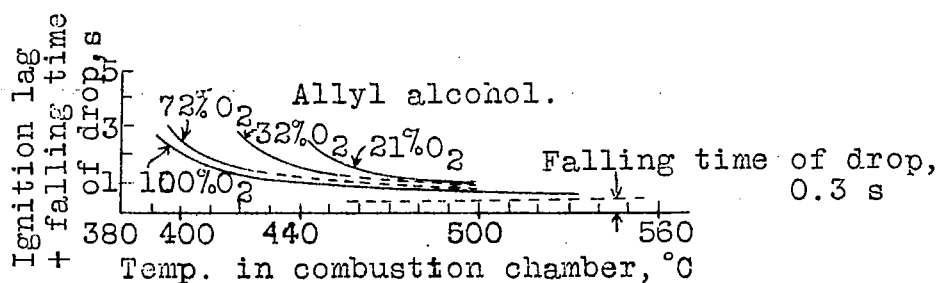
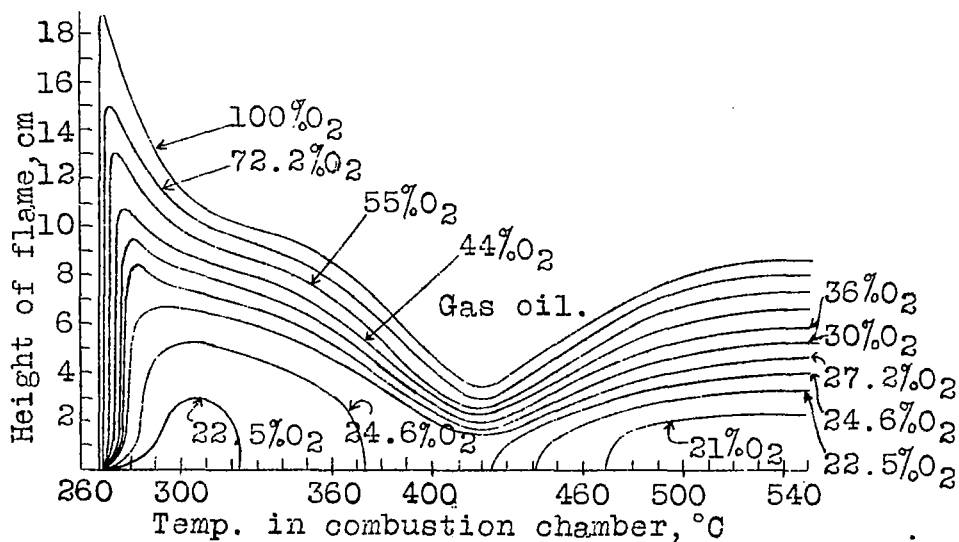
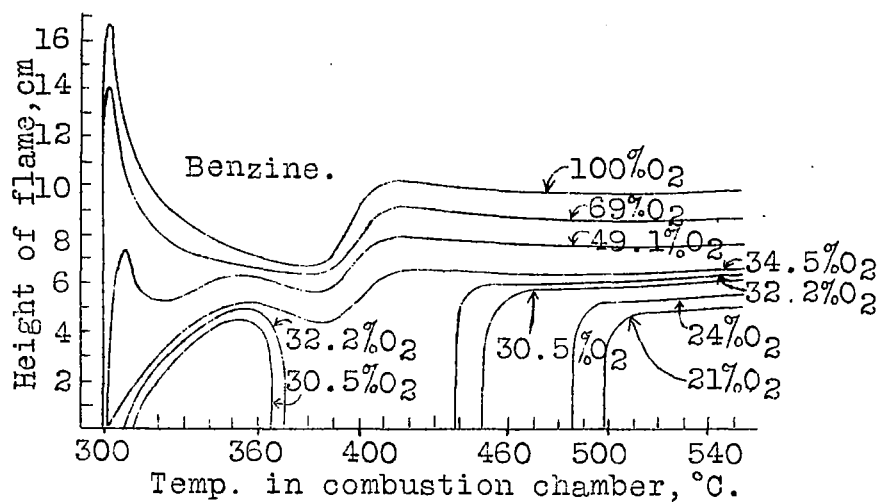
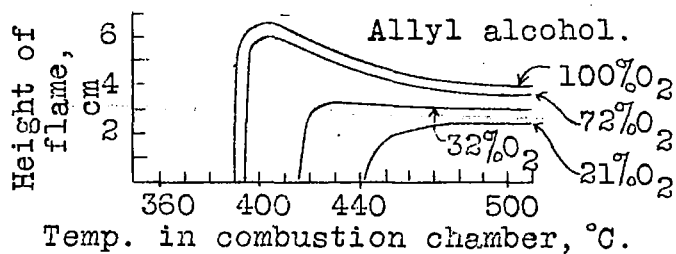


Fig.3-6 Effect of oxygen content on ignition tempature, at 1 atmosphere.



Figs.7-9 Effect of oxygen content on ignition at 1 atmosphere. Weight of drop = 3 mg.



Figs.10-12 Effect of oxygen content on ignition strength at 10 atmosphere.

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